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Key Issues Hindering a Practical Lithium-Metal Anode

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The sluggish progress of battery technologies has drastically hindered the rapid development of electric vehicles and next-generation portable electronics. The lithium (Li) metal anode is critical to break the energy-density bottleneck of current Li-ion chemistry. After being intensively studied in recent years, the Li-metal field has developed new understanding and made unprecedented progress in preventing Li-dendrite growth and improving Coulombic efficiency, especially through development of advanced electrolytes and novel analytical tools. In this Opinion, we revisit the controversial issues surrounding Li metal as an anode based upon recent advances, revealing the underlying cause of Li-metal failure and the true role of ‘solid electrolyte interphase’ in Li-metal anodes. Finally, we propose future directions that must be taken in order for Li-metal batteries to become commercially viable.

Highlights

Advanced liquid electrolytes can achieve dense Li deposition with a Coulombic efficiency (CE) of approximately 99%.

New characterization tools, including cryogenic electron microscopies and quantitative chemical analytical tools, have enhanced the current understanding of Li failure mechanisms.

Quantification of inactive Li reveals that the underlying cause of low CE in Li-metal anodes is the large amount of unreacted metallic Li.

Rise of the Lithium-Metal Anode

Rechargeable batteries have markedly reshaped our lives – from electric vehicles to portable electronic and optoelectronic devices. For a battery anode, lithium (Li) metal is considered the ‘Holy Grail’ because of its extremely low density (0.534 g cm^{-3}), ultra-high theoretical capacity (3860 mAh g^{-1}), and exceptionally negative electrochemical potential (-3.04 V vs. standard hydrogen electrode) [1]. The Li-metal anode was first adopted in the TiS_2 -Li prototype in 1976 [2,3], but was soon replaced by **intercalation compounds** (see [Glossary](#)) like graphite (C) because of severe capacity fading and potential explosion hazards resulting from dendritic Li growth [4]. Since C/LiCoO₂-based Li-ion batteries delivered an energy density of 120–150 Wh/kg, twice that of the state-of-the-art Ni–Cd batteries at the time [3], Li-ion batteries rapidly supplanted Ni–Cd in the battery market, becoming the prevalent technology. Since then, Li-ion chemistry research has thrived, with significant effort expended toward further increasing energy and power density. Meanwhile, the use of Li metal as the anode material has also gradually resuscitated after the 20 years of dormancy since its initial introduction. Around 2010, prospering electric-vehicle and consumer-electronic markets urgently demanded development of high-energy-density storage devices, triggering explosive research on Li-metal batteries to achieve an energy density of 500 Wh/kg or higher in the form of high-Ni NMC-Li or S-Li batteries [5]. [Figure 1](#) summarizes the number of papers published with a keyword of ‘lithium metal battery’ over the past 40 years, clearly demonstrating the intense interest in Li-metal batteries.

Current Li-metal-battery research is primarily focused on strategies to alleviate Li-dendrite formation, improve **Coulombic efficiency** (CE), and better understand plating/stripping through advanced characterization methods and theoretical modeling. These efforts have been systematically summarized in the recent reviews [6–11]. Among these achievements, it is important to highlight that dense Li deposition with a CE of approximately 99% is currently readily obtainable by employing electrolytes of high salt concentration [12–16] or localized high-concentration electrolytes [17,18].

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Number of papers on lithium metal battery

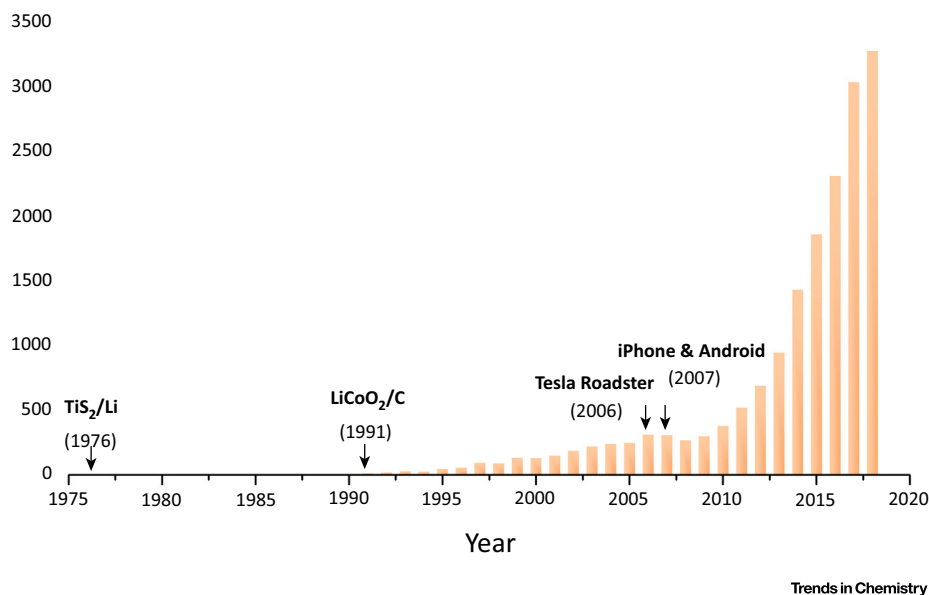


Figure 1. The Number of Papers on Li-Metal Batteries Published Each Year since Its First Introduction in 1976. A total number of 17 376 of papers have been published. Statistics from the Web of Science by searching keywords 'Lithium Metal Battery' (as of December 1, 2018).

Another key achievement of note is the use of **cryogenic electron microscopy** (cryo-EM) to visualize the nanostructure of the electrochemically deposited Li metal (EDLi) and mysterious **solid electrolyte interphase** (SEI) [19–21], affording a powerful tool to correlate nanostructure with performance and optimization strategies. Based on these exciting achievements, it is an optimal time to revisit current understanding of the Li-metal anode and review several outstanding challenges. In this Opinion, we discuss controversial issues associated with Li-metal anodes, evaluate proposed solution strategies, and propose future directions to realize a practical Li-metal anode.

Main Challenges with Li Metal: Dendrite Formation or Low Coulombic Efficiency?

It is widely accepted that Li-dendrite formation and low CE are two primary obstacles hindering Li-metal batteries [22]. In addition, other challenges associated with Li-metal anodes include volume expansion, poor cycle life, capacity fading, increased overpotential, and potential safety hazards. It is commonly thought that Li dendrites can mechanically pierce the separator, causing a short in the cell that potentially results in thermal runaway and explosion [3]. Figure 2A shows an Li-dendrite model that has been widely spread to illustrate the potential dangers of Li dendrites. This dendritic morphology was originally observed in a beaker cell via optical microscopy [22–24]. However, in real coin cells and pouch cells, this morphology has rarely been observed or reported. Instead, whisker-like Li deposits are commonly observed in commercial carbonate-based electrolytes and even solid-state batteries (Figure 2B), due to the heterogeneous nature of SEI layers, ion concentration, and local current density [25]. These Li whiskers interweave parallel to the separator (rather than perpendicular); only a perpendicular whisker can penetrate the separator and potentially cause a cell short. Moreover, chunky Li deposits with large granular size (Figure 2C) have been observed in many recently developed advanced electrolytes. Based on these findings,

Glossary

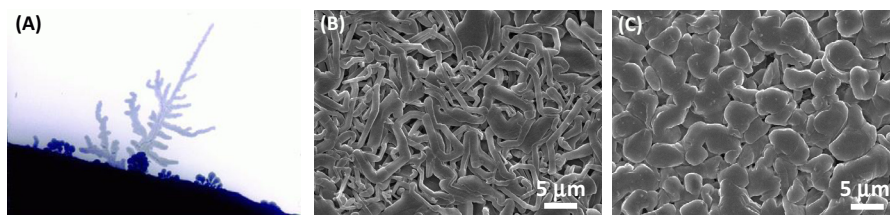
Coulombic efficiency (CE): also known as Faraday efficiency; it describes the efficiency with which charge is transferred in a system facilitating an electrochemical reaction. In a closed secondary battery system, the CE directly reflects the battery cyclability.

Cryogenic electron microscopy (cryo-EM): an electron microscopy technique applied on samples cooled down to cryogenic temperatures. This technique significantly reduces the electron beam damage on fragile samples and has been widely adopted in structure biology field to obtain atomic-resolution images. Recently, this technique has been introduced to the battery field and serves as a powerful tool to investigate the nature of extremely beam-sensitive lithium metal and SEI.

Intercalation compounds: compounds with layered structures that can host the reversible insertion of molecules or ions into the material. Common intercalation electrode compounds include graphite (anode), TiS_2 (cathode), layered oxides (cathode; e.g., LiCoO_2 and $\text{LiNi}_{0.8}\text{Mn}_{0.1}\text{Co}_{0.1}\text{O}_2$).

Solid electrolyte interphase (SEI): the interface between the electrode and electrolyte. It forms from the (electro)chemical reaction between the electrode and electrolyte, and the electrochemical decomposition of electrolyte, ensuring the kinetic stabilization of electrode–electrolyte interfaces. It remains conductive to ions but insulates electrons.

Titration gas chromatography (TGC): a new analytical method used to quantify trace amount of metals. It is a combination of protic solvent titration and quantification of H_2 amount by gas chromatography. The amount of metals can be calculated from the H_2 amount.



Trends in Chemistry

Figure 2. The Morphologies of Electrochemically Deposited Li under Different Conditions. (A) The famous optical microscope image representing Li dendrites [22]. (B) Whisker-like Li deposited in commercial carbonate electrolyte [1 M LiPF₆ in ethylene carbonate (EC)/ethyl methyl carbonate (EMC), 3:7 with 2% of vinylene carbonate (VC), 0.5 mA/cm², 1 mAh/cm²]. (C) Chunky Li with a large granular size formed in high-concentration ether-based electrolyte [4 M LiFSI in 1,2-dimethoxyethane (DME), 0.5 mA/cm², 1 mAh/cm²].

it is misleading to continue ascribing the major problem associated with Li-metal anodes to dendritic growth and its resultant internal short circuit/thermal runaway. Lu and colleagues [26] have also refuted the dendrite-penetration-related failure mechanism by scanning electron microscopy analysis of an Li anode cross section after 100 cycles. Undoubtedly, the Li dendrites, or more precisely Li whiskers, play a critical role in affecting Li-metal battery performance. However, it is likely via other avenues (i.e., increasing surface area and/or causing large volume expansion) rather than directly causing a short circuit.

We believe that the primary issue with Li-metal stems from the low CE, which directly reduces the battery cycle life. As cycling proceeds, both fresh Li metal and electrolyte are consumed continuously, forming inactive Li (provided that the cycle CE is <100%). Thus, cycle life and stability in Li-metal cells are directly proportional to the amount of excess Li and electrolyte [27]. However, the CE of Li metal in conventional carbonate electrolytes is less than 90%, indicating that most Li-metal cells fail via consumption of active Li or depletion of electrolyte (rather than short circuiting caused by Li whiskers). Even for advanced electrolytes that enable highly efficient Li plating/stripping with CE of approximately 99%, the 1% inefficiency remains problematic. To achieve a desired cycle life, excess amounts of fresh Li and electrolyte are needed, rendering it difficult to further improve the cell-level energy density. Thus, it is becoming inescapable to improve the CE of Li metal to extend the cycle life of the Li-metal batteries.

Inactive Li Formation Causes Low CE: SEI Li⁺ or Unreacted Metallic Li?

Low Li-metal CE stems from the loss of active Li as it forms the SEI and unreacted metallic Li, which together comprise inactive Li (also known as ‘dead’ Li). SEI formation is a result of the (electro)chemical reaction between highly reactive Li metal and the electrolyte (Box 1), whereas unreacted metallic Li is isolated from the electronically conductive network during stripping by the insulating SEI, thus becoming inactive [28–30].

The importance of the SEI has been reviewed exhaustively [11,31,32]; however, quantitative characterization of SEI properties remains elusive, including chemical composition, nanostructure, and mechanical properties. This is partly due to the brittle and heterogeneous nature of the SEI. It is generally believed that dramatic volume changes yield fractures in the SEI during Li stripping/plating [10]. This fracturing results in continuous SEI formation that consumes both the active Li and electrolyte. This process is further accelerated by growth of porous Li whiskers. With this in mind, many researchers attribute the continuous formation of SEI as the primary reason for capacity loss and low CE, without further quantitative verification [33].

Box 1. Key Electrochemical Reactions in an Li-Metal Battery

During plating in an Li-metal battery, Li^+ deposits on fresh Li. In commercial carbonate-based electrolytes, Li deposits exhibit whisker-like morphology. During stripping, Li dissolves into the electrolyte and becomes Li^+ . If the dissolution first occurs at the base of the Li whiskers, the top part will disconnect from the electronically conductive framework and thus becomes electrochemically inactive, forming inactive Li (consisting of SEI and unreacted metallic Li wrapped by the insulating SEI; Figure 1).

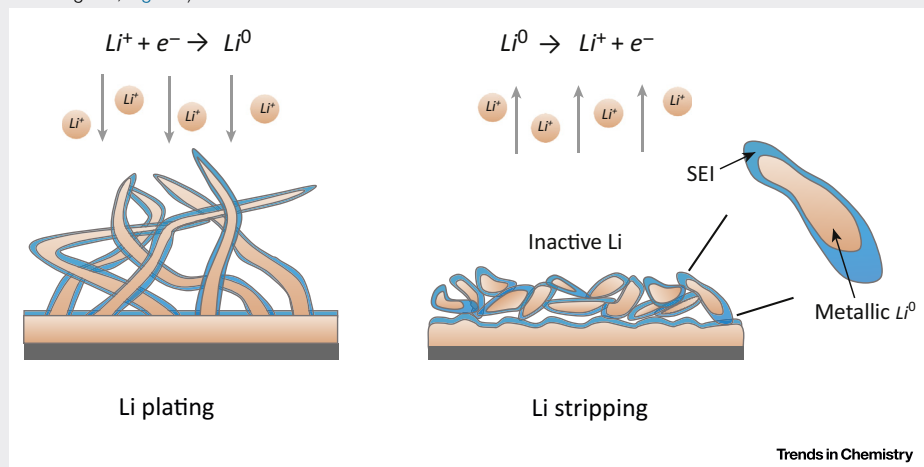


Figure 1. Schematic of Electrochemical Li Plating/Stripping, Dendrite Formation, and Inactive Li Formation.

However, it was recently reported that this picture is not correct following quantification of both the SEI Li^+ and unreacted metallic Li after stripping via the recently developed **titration gas chromatography** (TGC) [34]. Importantly, TGC results reveal that the capacity loss of Li-metal anodes is primarily dominated by unreacted metallic Li that is trapped by the insulating SEI. The overall SEI Li^+ amount in the inactive Li remains almost identical and at a relatively low amount under different testing conditions. This suggests that the main loss of CE in Li-metal batteries does not come from SEI formation but rather from the unreacted metallic Li [34]. The capacity loss from forming SEI has been overblamed for decades. Although the amount is low, we still want to emphasize that the SEI cannot be overlooked since its chemical and mechanical properties directly dictate the surface properties of the EDLi, directly affecting the dynamic Li plating and stripping process. Much work is still needed to correlate the SEI properties with the electrochemical behavior and performance of Li-metal anodes.

Strategies for Improving Coulombic Efficiency

Many strategies have been proposed to improve CE, including electrolyte engineering [35–37], use of a 3D host [38,39], separator modification [40,41], and artificial SEI engineering [42,43]. For example, atomic/molecular layer deposition has been shown to be an effective approach to enhance the CE and decrease the formation of ‘dead’ Li [44–46]. Among these strategies, the most effective and promising is developing new electrolytes that enable both high-efficiency Li-metal and stable high-voltage cathode operation. Dense Li deposition with a CE over 99% is readily obtained [13,14,16,17]; however, a 99.97% CE is required for a commercially viable Li-metal anode that must undergo 1000 cycles [47].

To close the gap of less than 1% CE loss per cycle further, we must fully understand the growth and failure mechanism of Li metal in both liquid and solid-state electrolytes by employing state-of-the-art characterization tools. For example, operando optical microscopy [48] and *in situ* transmission electron microscopy (TEM) [49] were combined to probe the dynamic growth of Li dendrites on a wide range of

length and time scales. In particular, cryo-EM eliminates detrimental beam damage on fragile Li metal and affords nanostructure visualization. Aside from microscopy, other techniques are also needed to quantitatively probe the structure and amount of Li metal/SEI, such as TGC [34]. Significant advances in characterization are helping researchers get unprecedentedly close to truly understanding the Li-metal failure mechanism and rationally overcoming the previously stated obstacles for Li metal.

Recently, Meng and colleagues [34] used cryo-TEM to observe the nanostructure of inactive Li, revealing that unreacted metallic Li is trapped by the SEI. Further, it was shown that the unreacted metallic Li amount is closely correlated with the Li-deposit microstructure. A large quantity of unreacted metallic Li is easily trapped in tortuous matrix of the whisker-like Li, resulting in a low CE. By contrast, a smaller quantity of unreacted metallic Li is present following stripping large chunky Li deposits with lower porosity. Consequently, they assert that whisker-like Li is an undesired microstructure that accelerates formation of inactive metallic Li as well as infinite volume expansion, thereby yielding low CE (rather than assigning potential safety concerns to Li-dendrite formation). Therefore, they propose that chunky Li deposits are the preferred microstructure for maintaining a suitable electronic connection between deposited Li and the current collector in a limited volume space. In addition, this preferred morphology implies that significantly less unreacted metallic Li will be trapped in the SEI, thereby affording an improved CE. Thus, we anticipate that strategies to bias Li deposits to form a columnar chunk morphology will be effective in further improving CE and confining the volume expansion. Figure 3 (Key Figure) summarizes the cause and solutions for Li-metal problems.

Key Figure

The Cause and Potential Solution for Li-Metal Issues

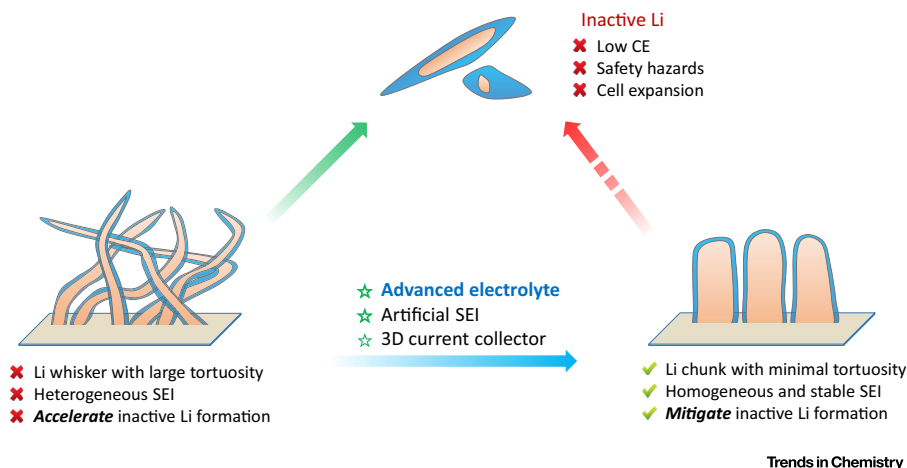


Figure 3. The continuous formation of inactive Li is the direct cause of low Coulombic efficiency (CE), safety hazards, and cell expansion in Li-metal batteries. Li whiskers with large tortuosity and heterogeneous solid electrolyte interphase (SEI) will facilitate the inactive Li formation and cause the series of problems. Conversely, if the deposited Li possesses a chunky morphology with minimal tortuosity and homogeneous SEI, inactive Li formation will be significantly reduced resulting in high CE [34]. To do so, advanced electrolyte engineering will likely be a primary method, with the assistance of artificial SEIs and 3D current collectors [34].

Concluding Remarks and Future Perspectives

In this Opinion, we demonstrate that the major problem of Li-metal anodes is low CE rather than Li-dendrite formation. Most Li-metal cells fail due to the consumption of active Li or depletion of electrolytes rather than the short circuit caused by Li dendrites/whiskers. The loss of CE is largely dominated by the formation of unreacted metallic Li rather than the SEI, which is related to the microstructure of Li deposits [34].

In the future, research effort should be devoted toward reducing the amount of unreacted metallic Li through tuning the nanostructure and microstructure of deposited Li during both the plating and stripping processes. An ideal Li deposit should have a columnar morphology [34]; the SEI layer should be homogeneous in components and their distribution with sufficient mechanical strength and elasticity; the deposited Li volume should be close to the theoretical value. Advancing electrolytes will undoubtedly be the most effective solution to generate these large Li chunks with minimal tortuosity. A combination of the 3D substrate (helping maintain suitable electronically conductive pathways) and an artificial SEI with all the desired properties may also be required to enhance the structural connection for electrons and ion transfer through the SEI, which all together could potentially realize the CE goal of more than 99.97%.

To carefully carry out these strategies, a thorough understanding of SEI properties is the key. With advances in cryo-EMs, we are now able to correlate the nanostructure of Li metal with the electrochemical performance under various conditions. Operando/*in situ* cryo-EM should be soon established to probe the dynamic processes of Li metal and SEI during plating and stripping. Although the SEI amount is low [34], it plays an important role in altering and affecting the Li behavior. Many interesting questions remain (see Outstanding Questions). Answering these questions are of vital importance toward rationally eliminating the 1% of CE loss to ultimately make the Li-metal batteries commercially viable.

Lastly, we advocate the field to follow standardized testing protocols for more effective knowledge transfer. As mentioned before, the cycle life and cycling stability in an Li-metal cell are directly proportional to the excess amount of Li and of the electrolyte. Many reported cycling data are based on a large excess of electrolyte and effectively an infinite excess amount of Li metal in coin cells; these methodologies do not accurately reflect the true performances of the reported strategies. Battery R&D has reached a point where scientific research advances are evaluated and assessed by how rapidly and reproducibly they can be deployed in a commercially relevant design. This extremely demanding trend itself is a double-edged sword as it might constrain the creativity of the scientists, but if successful, it will accelerate the realization of next-generation batteries. When developing strategies to improve the CE in Li-metal anode, we advocate researchers to rise up to the tough technical challenges, apply and report strict standards, including high mass loading of active cathode materials (≥ 4 mAh/cm²), proper current density (> 0.5 mA/cm²), lean electrolyte (≤ 3 g/Ah), and a limited excess amount of Li metal (< 50 μ m thickness), to truly evaluate if these strategies are actually effective for a practical rechargeable Li-metal battery.

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Outstanding Questions

What is the ideal structure of the solid electrolyte interphase (SEI)? How do we achieve this structure?

How do Li ions diffuse through the SEI?

Will the Li refill the as-formed SEI shells in subsequent cycles?

How do we achieve ideal columnar Li deposits as opposed to whisker-like formations?

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